The Migration and Monitoring of Viscous NAPLs (Coal Tar & Creosote) in the Subsurface

Richard Jackson,
INTERA Engineering Ltd, Heidelberg, Ontario, Canada

ABSTRACT

The much higher viscosity of viscous NAPLs, such as creosote and coal tar, relative to groundwater – usually an order of magnitude at least – greatly complicates the understanding of their mobility and monitoring at contaminated sites. These NAPLs can remain mobile – but with very low seepage rates here referred to as '*creeping flow'* – for many decades after the closure of facilities in which they were generated (coal tar) or used for wood preserving (creosote). . Creeping flow means that pumping monitoring wells may not cause mobile viscous NAPL to enter the well with ease because of [1] a negative feedback loop with respect to their relative permeability with respective to groundwater and [2] the wetting state of the geological materials within which they are present. Examples of this creeping flow and monitoring difficulties are given from sites in British Columbia and Florida and an example of coal tar removal by polymer-surfactant flooding in Illinois is presented.

RÉSUMÉ

La créosote, le goudron et autres liquides visqueux (NAPL en anglais) se comportent dans les sols alluvionnaires de façon bien différente de ceux moins visqueux, par exemple, l'essence et les dissolvants chlorés. Leur comportement unique se doit à l'interaction de leurs parameters chimio-physiques: une densité souvent plus importante que celle de l'eau, une viscosité bien plus élevée que l'eau et une tension interfaciale qui produit un coefficient initial d'extension positif aux interfaces de l'air, de l'eau et de l'huile. Il s'ensuit que ces huiles visqueuses se répandent lentement et entraînent la contamination à longue terme de certains sites qui ont utilisé ces liquides immiscibles, et des cours d'eau adjacents. Deux études de la migration de ces huiles visqueuses dans sites en Colombie Britannique et en Floride sont présentés. Les résultats indiquent que cette huile visqueuse peut se répandre pendant plusieurs années avant de déboucher dans des fleuves à des niveaux plus bas où dans un puit de captage des eaux souterraine.

1 INTRODUCTION

The slow migration of viscous non-aqueous phase liquids or NAPLs, such as creosote or coal tar or heavy fuel oils, often makes it appear that the NAPLs are stationary in the subsurface. Rather it is often the case that they are undergoing creeping flow, i.e., at low velocities. This issue has been examined in the context of a brownfields site in British Columbia by Jackson et al. (2006).

Therefore the misidentification of mobile viscous NAPL is a common occurrence and, therefore, many years after the closure of industrial facilities, such as wood-preserving sites, fuel oil terminals and coal-gasification facilities, NAPLs appear in nearby waterways or in pumping or monitoring wells for reasons that geoenvironmental engineers and hydrogeologists find puzzling.

The purpose of this paper is to help facilitate the understanding of this issue as it undoubtedly has implications for former and current industrial sites in Cape Breton, elsewhere in Nova Scotia and in New Brunswick.

2 PROCESSES CONTROLLING THE MIGRATION OF VISCOUS NAPLS

2.1 Two-phase flow

In a two-phase geosystem of ground water (gw) and NAPL or oil (o), the Darcy flux of water and oil flow, q_{gw} and q_o, is controlled by the relative permeability functions, k_{rgw} and k_{ro}, and the viscosity difference between NAPL and water (e.g., Dake 1994):

[1a]
$$q_{gw} = -\frac{kk_{rgw}}{\mu_{gw}} A \frac{\Delta p_{gw}}{\Delta L}$$

[1b]
$$q_o = -\frac{kk_{ro}}{\mu_o} A \frac{\Delta p_o}{\Delta L}$$

where k is the intrinsic permeability of the soil or rock (m^2), μ_w and μ_o are the absolute or dynamic viscosities of the water and oil phases (Pa·s), A is the cross sectional area of flow through the porous medium and Δp/ΔL is the pressure gradient for each of the phases.

Considering equations 1a and 1b, because k and A are common to both equations and assuming $\Delta p_w/\Delta L \approx \Delta p_o/\Delta L$, then the two fluxes, q_w and q_o, are a function of their relative permeabilities and the fact that for viscous oils $\mu_o >> \mu_w$. Figure 1 shows typical relative permeability curves for NAPL (oil) and ground water. The abscissa is given in water saturation as a volume fraction of the pore space; the ordinate is the relative permeability that also varies from 0 to 1.0.

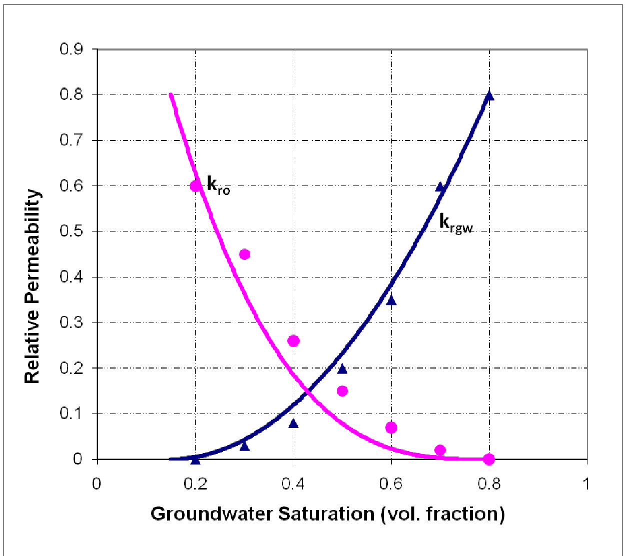

Figure 1. Relative permeability functions for NAPL (k_{ro}) and groundwater (k_{rgw}) referenced to the groundwater saturation, i.e., fraction of pore volume occupied by groundwater as opposed to NAPL (from Jackson et al. 2006).

The potential for lateral migration of creosote or coal tar NAPL beneath the water table is much more difficult to ascertain by well testing because of the effect of the high viscosities of these NAPLs on their flow to wells. Assuming gravity drainage can be ignored after a cone of depression has developed and stabilized, consider the case of lateral flow of ground water (μ_w = 1E-03 Pa·s) and a viscous NAPL (μ_o = 20E-03 Pa·s) to a purpose-built NAPL extraction well that is installed at the base of an alluvial aquifer beneath which is a capillary barrier. The creosote flux will be limited by its high viscosity relative to the groundwater flux during pumping from the well and k_{ro} – the relative permeability function for NAPL shown in Figure 1 – will decline and the groundwater saturation increase, all other conditions being equal.

Consequently, when creosote or coal tar are produced at a well, flow of additional NAPL to the well is relatively slow compared with the much less viscous groundwater. Therefore, the groundwater saturation in the pore spaces adjacent to the well increases with extraction of creosote and groundwater from the well causing k_{rw} – the relative permeability function for groundwater shown in Figure 1 – to increase and k_{ro} to decrease yielding $k_{ro}/\mu_o \div k_{rw}/\mu_w << 1$, and $q_w >> q_o$. Thus the feedback between viscosity and relative permeability of creosote results in ever decreasing creosote flow to the well and a higher ratio of water-to-creosote production. Low rates of total fluid extraction can be effective in maximizing creosote recovery and minimizing ground water recovery but must be continued over the long term. This creeping flow may well require testing of a potentially-contaminated aquifer by extraction for several months at low flow rates.

2.2 Gravity Drainage of NAPL at the Water Table

In two-phase (water/NAPL), water-wet systems, residual NAPL exists primarily as discontinuous blobs within a single pore or several adjacent pore bodies (Chatzis et al. 1983; Schwille 1989; Conrad et al. 1992; Powers et al. 1992). Generally, the residual NAPL will reside in the larger pores where capillary forces are smallest. Wilson et al. (1990) observed residual NAPL saturations ranging from 14% (0.14) to 30% (0.30) in unconsolidated sands and possibly higher in heterogeneous sand packs.

In three-phase systems (i.e., air-water-NAPL), the presence of air can alter the distribution of the NAPL dramatically. A schematic of the air-water-NAPL interface is depicted in Figure 2. The spreading tendency can be evaluated by performing a force balance on the interfacial tensions shown in Figure 2. If the air-water interfacial tension (σ_{aw}) is greater than the vector sum of the NAPL-water interfacial tension (σ_{nw}) and the contribution of the air-NAPL interfacial tension (σ_{an}), then the NAPL will tend to spread on the air-water interface:

$$[2] \qquad \sigma_{aw} \cos\alpha - \sigma_{nw} \cos\varepsilon - \sigma_{an} \cos\beta > 0$$

NAPL spreading condition

where α, β and ε are the wetting angles as shown in Figure 2. This relationship is often simplified for the case of $\alpha = \beta = \varepsilon = 0°$, and the condition for oil spreading is defined in terms of the initial spreading coefficient (S) as follows (e.g., Charbeneau 2000, p. 473):

$$[3] \qquad S \equiv \sigma_{aw} - \sigma_{nw} - \sigma_{an}$$

When the spreading coefficient is positive, the NAPL will spontaneously spread in the form of a thin film between the air and water phases. Under these conditions, the residual NAPL saturation tends to be much lower than that for a two-phase system (Wilson et al. 1990).

Three-phase systems have significantly lower residual NAPL saturations than the two-phase system of water and the same NAPL and may promote the migration of viscous NAPLs. These lower three-phase residual saturations for the same aquifer material under otherwise identical conditions (i.e., except for air entry) were documented over 15 years ago in the experimental studies of a lighter-than-water NAPL (LNAPL) by Wilson et al. (1990) and of a denser-than-water NAPL (DNAPL) by Schwille (1989). Mercer and Cohen (1990) summarized this significant difference in residual saturations for NAPL as follows: the range in the vadose (or three-phase) zone is 0.10 to 0.20, whereas the range in the ground-water (or two-phase) zone is 0.15 to 0.50. Table 2 shows the data of Wilson et al. (1990) and Schwille (1989) for two- and three-phase conditions of residual saturation.

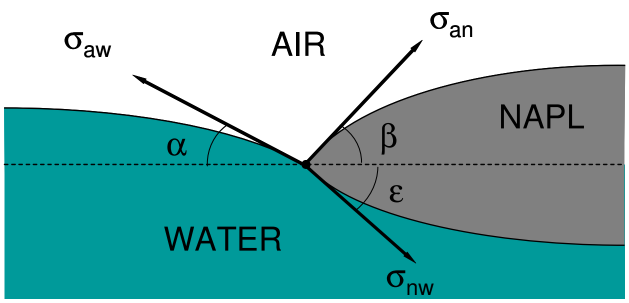

Figure 2. Schematic of air-water-NAPL interface (from Jackson et al., 2006).

System	Condition	Saturation (%) or Retention Capacity (L/m^3)	Reference
Air + Soltrol + water	3-phase	9.1 ± 2.2 %	Wilson et al. (1990)
Soltrol + water	2-phase	27.1 ±1.7 %	Wilson et al. (1990)
Air + CHC + water	3-phase	30 L/m^3	Schwille (1989)
CHC + water	2-phase	50 L/m^3	Schwille (1989)

Table 2: Residual saturations in two- and three-phase systems comprised of clean sand with K=1E-4 m/s.

The specific volume of NAPL remobilized (H_m) by a decline in the water table (Δz) is simply:

$$H_m = \varphi\left(S_{ors} - S_{orv}\right)\Delta z \tag{4}$$

where φ is porosity, S_{ors} is the two-phase or groundwater zone residual NAPL saturation and S_{orv} is the three-phase or vadose zone residual NAPL saturation.

Figure 3 shows how much NAPL drains downward following a one-meter drop for given two- and three-phase residual saturations. Using Wilson et al.'s (1990) values S_{ors} = 27%, S_{orv} = 9%, and φ = 35%, Equation (1) yields a specific volume of 0.35(0.27-0.09)1 = 0.063 m^3 or 63 L of NAPL per cubic meter of aquifer that is dewatered.

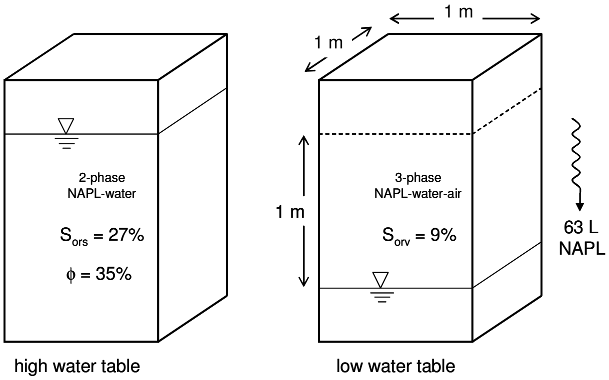

Figure 3. Schematic of gravity drainage of viscous NAPL due to water-table lowering.

3 TWO CASE HISTORIES

3.1 Creosote Contamination of the Fraser River, British Columbia

Wood-preserving operations at the KICL site near Vancouver B.C ended in the early 1980s and the site was re-developed as a warehouse for handling newsprint brought by barge, rail and truck. It was unfortunate that the various site investigations that were undertaken in the early 1980s failed to reveal the extent and mobility of the creosote contamination present in-situ before the construction of the warehouse proceeded on the site. Continued creosote migration into the Fraser River for 15 years following site de-commissioning lead to regulatory actions initiating ground-water extraction, subsequent building settlement, and finally litigation over the recovery of costs for the $35 million remediation program.

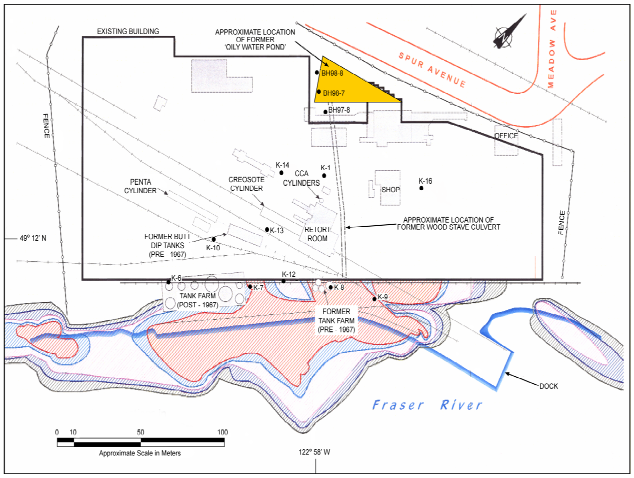

Figure 4. Brownfields site, Burnaby, British Columbia

Figure 4 shows the site with the outlines of the former wood-preserving operations and of the new warehouse building indicated and the shaded area indicating creosote seepage into the bottom sediments of the Fraser River. The site is typical of those along the Fraser

River Delta in that it is underlain by a thick sequence of fluvial sands and overbank silts and clay. This is an example of one site in which long-term seepage of a viscous NAPL continued for long after the site was closed. Creeping flow of creosote was responsible for continuing contamination of the Fraser River fishery.

3.2 Creosote contamination of the Floridan Aquifer

The Floridan aquifer is the principal water supply for much of the State of Florida. In the city of Gainesville it supplies 180,000 residents including the students at the University of Florida. It is a karstic Eocene-Oligocene limestone that is overlain by 40 m of the Hawthorn Group sediments that form an aquitard and a 10 m surficial (quartz) sand aquifer. At the Koppers Superfund site in Gainesville, the surficial aquifer is heavily contaminated by creosote that has penetrated through the Hawthorn aquitard and has contaminated the Floridan Aquifer. Whether this contamination is by DNAPL penetration or by aqueous-phase migration is contested, however it appears that both the viscous NAPL and associated dissolved phase contamination are currently present in the Floridan Aquifer some 3 km from the City well field.

Figure 5 shows creosote migrating through the Hawthorn Group clays. Similar penetration was observed by Feenstra and Cherry (1996) in the Winnipeg clays.

Figure 5: creosote penetration of a clay aquitard, Koppers Superfund site, Gainesville, Florida

The penetration of the 40 m thick aquitard by creosote was unexpected in Florida as it would be in many places that rely on deep aquifers that are believed protected by overlying clay-rich sediments. Figure 6 shows the conceptual model of the site prepared by a reputable consulting firm in 1993. Note how the viscous DNAPL is considered stationary at the base of the surficial aquifer. This perception is very much linked to the high viscosity of the NAPL such that its mobility is difficult to discern.

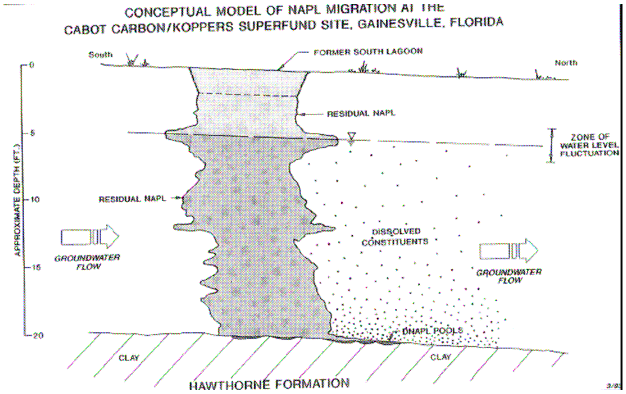

Figure 6: Early conceptual model (1993) of creosote NAPL migration and trapping at the Gainesville Superfund site. As Figure 5 shows, the NAPL actually penetrated the clay of the underlying Hawthorn Formation.

The fact that this viscous NAPL failed to appear in most monitoring wells – similar behaviour was noted in the case of the British Columbia site as well – does not mean that the NAPL itself is stationary but that there is no *a priori* reason why a high-viscosity NAPL that tends to wet the soils through which it migrates should necessarily penetrate a monitoring well.

4 VISCOUS NAPLS AND MONITORING WELLS

The migration of viscous NAPLs is governed by the laws of multiphase flow and trapping that have been introduced above. This means that for a viscous NAPL to penetrate an otherwise clean soil, it must exceed the entry pressure of the pores of that soil. The entry pressure, P_e, is that pressure required to overcome the capillary resistance of a water-wet pore throat system to its penetration by a non-wetting fluid, e.g., a viscous NAPL. The pressure that the viscous NAPL can exert is simply the product of its fluid density, gravitational acceleration and the pressure head exerted by the continuously-connected column of the NAPL. Therefore, water-wet pores surrounding a monitoring well are penetrated by viscous NAPL when the NAPL pressure exceeds the entry pressure of the pore system constituting the well screen, sand pack and any silt in the well itself, i.e., the “well/soil system”.

The height of the NAPL column is critical in propagating the penetration of the NAPL to greater depths. Because the NAPL pressure head will increase with its height, the greatest NAPL pressure is exerted at the base of the

NAPL column provided the column remains continuously connected throughout. Figure 7 shows a blob of creosote NAPL migrating through a surficial sand aquifer like that shown in Figure 6, but which will not penetrate the extraction well because the entry pressure is much higher than the pressure that can be exerted by the pressure of the DNAPL in the shallow aquifer. The necessary condition for the DNAPL to enter the extraction well is that the fluid pressure exerted by the DNAPL must exceed the entry pressure of the well/soil system.

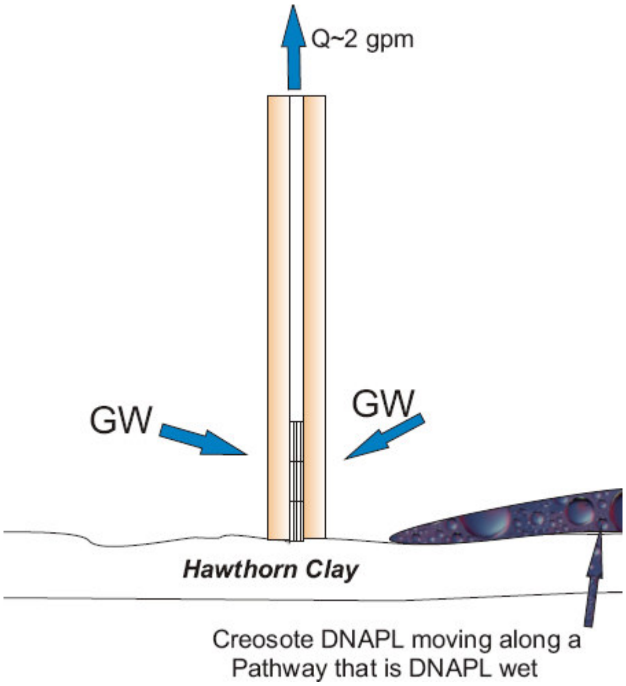

Figure 7: In the shallow aquifer, a viscous DNAPL migrates along the top of a capillary barrier – the Hawthorn Clay shown in Figure 5 – but does not enter the extraction well pumping 2 gallons per minute.

Once a DNAPL has wetted a path through the subsurface, the entry pressure for fresh DNAPL to follow this DNAPL-wet path is zero, although the permeability of the DNAPL-wet soil may inhibit much penetration. But the entry pressure to penetrate a well screen that is newly installed nearby is not zero and the DNAPL will not obligingly enter the well just because it is installed where DNAPL is suspected to be migrating. For the case of chlorinated solvents, which have a viscosity less than that of groundwater, penetration is much easier, but viscous NAPLs such as creosote, coal tar, mercury and heavy fuel oils do not penetrate water-wet sediments and soils readily.

In the case shown in Figure 8, the NAPL migrates along an already NAPL-wet flow path, perhaps a paleochannel of coarse sand or a joint set in bedrock. To enter the well, the NAPL has to overcome the capillary resistance exhibited by water-wet pores between the NAPL and the well screen for which the capillary resistance is > 0, whereas there is no capillary resistance to continued migration in a NAPL-wet pathway.

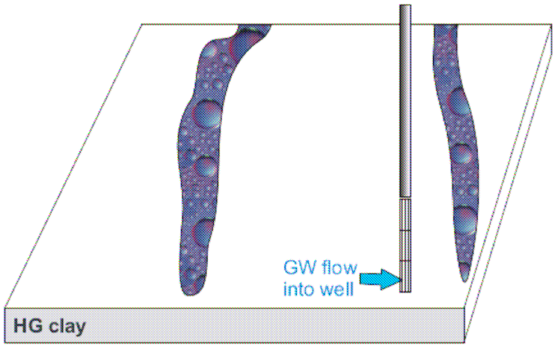

Figure 8: Viscous NAPLs such as creosote, coal tar, mercury and heavy fuel oils do not penetrate water-wet sediments and soils readily.

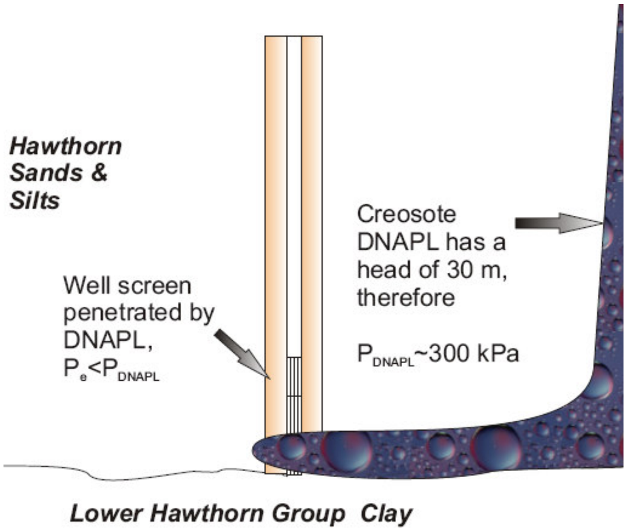

Figure 9: The blob of DNAPL shown in this figure is for the case of a 30 m high column of DNAPL in the sand and silts above the basal clay. In this case the well/soil system is penetrated by the DNAPL because the entry pressure is lower than the pressure exerted by the DNAPL at the base of the formation. This is the essential condition for the penetration of any well screen by an NAPL.

5 CONCLUSIONS

Viscous NAPLs, such as creosote and coal tar, behave very differently in the subsurface than do other NAPLs of lower viscosity, e.g., gasoline and chlorinated solvents.

1. They migrate by a process best described as *creeping flow* due to their high viscosity, which is often 10 or 20 times that of water. Their migration rate is very slow and often leads to the erroneous conclusion that they are stationary, i.e., trapped as residual NAPL.

2. Their migration path typically will follow a NAPL-wet pore system. In order to capture such NAPL in an extraction well, it is necessary for the NAPL to overcome the capillary resistance of uncontaminated soils to enter that well/soil system. Consequently, it is not necessarily the case that the NAPL can be induced to flow into an extraction well even with high pumping rates. Extraction is further complicated by the negative feedback to NAPL migration caused by its high viscosity and low relative permeability.

3. This negative feedback causes great difficulty in even sampling viscous NAPLs in wells. It is likely that slow rates of pumping over long periods of time – e.g., several weeks – are necessary to induce some NAPL migration into a monitoring well.

REFERENCES

Charbeneau, R. 2000. *Groundwater Hydraulics and Pollutant Transport.* Prentice Hall, Upper Saddle River, New Jersey.

Chatzis, I., Morrow, N.R., and Lim, H.T. 1983. Magnitude and detailed structure of residual oil saturation. *Society of Petroleum Engineers Journal*, **23**: 311-326.

Conrad, S.H., Wilson, J.L., Mason, W.R., and Peplinski, W.J. 1992. Visualization of residual organic liquid trapped in aquifers. *Water Resources Research*, **28**: 467-478.

Dake, L.P. 1994. *The Practice of Reservoir Engineering*. Elsevier, New York.

Feenstra, S. and Cherry, J. A. 1996. Diagnosis and assessment of DNAPL sites. *In Dense Chlorinated Solvents and Other DNAPLs in Groundwater*. *Edited by* J.Pankow and J.A. Cherry, Waterloo Press, Portland, Oregon, pp. 395-473.

Jackson, R.E., Dwarakanath, V., Ewing, J.E. and Avis, J. 2006. Migration of viscous non-aqueous phase liquids (NAPLs) in alluvium, Fraser River Lowlands, British Columbia. *Canadian Geotechnical Journal* 43: 694-703.

Mercer, J.W. and Cohen, R.M. 1990. A review of immiscible fluids in the subsurface: properties, models, characterization and remediation. *Journal of Contaminant Hydrology*, Vol. 6, pp. 107-163.

Powers, S.E., Abriola, L.M. and Weber, Jr., W.J. 1992. An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: steady state mass transfer rates. *Water Resources Research*, **28**: 2691-2705.

Schwille, F., 1989. *Dense chlorinated solvents in porous and fractured media, model experiments*, *Translated by* James F. Pankow. Lewis Publishers Inc., Chelsea, Michigan, p. 146

Wilson, J.L., Conrad, S.H., Mason, W.R., Peplinski, W., and Hagan, E. 1990. *Laboratory investigation of residual liquid organics from spills, leaks, and the disposal of hazardous wastes in groundwater*. EPA/600/6-90/004, U.S. Environmental Protection Agency, Ada, Oklahoma.